

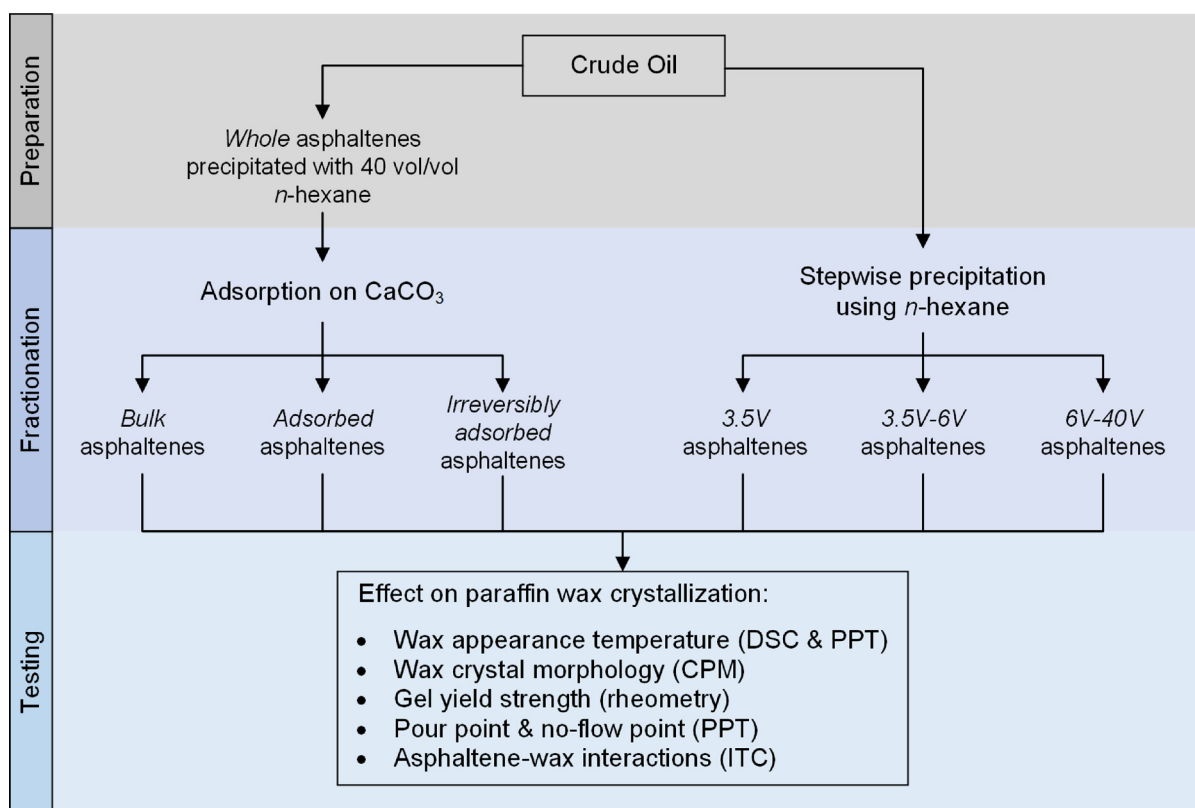
Asphaltene fractionation based on adsorption onto calcium carbonate: Part 3. Effect of asphaltenes on wax crystallization



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GRAPHICAL ABSTRACT



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ABSTRACT

Asphaltenes fractionation procedures were developed and tested in two preceding articles (doi: <https://doi.org/10.1016/j.colsurfa.2016.02.011>, doi: <https://doi.org/10.1016/j.colsurfa.2016.11.035>), and asphaltene fractions

Abbreviations: CPM, cross-polarized microscopy; DCM, dichloromethane; DSC, differential scanning calorimetry; FTIR, Fourier-transformed infrared spectrometry; ITC, isothermal titration calorimetry; MAC, maleic anhydride co-polymer; NIR, near-infrared spectroscopy; PEB, poly(ethylene-butene); PPD, pour point depressant; PPT, pour point tester; QCM, quartz crystal microbalance; THF, tetrahydrofuran; WAT, wax appearance temperature; WI, wax inhibitor

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Cross polarized microscopy (CPM)
Differential scanning calorimetry (DSC)

were characterized in terms of composition, adsorption and self-aggregation properties. In this article, the effect of asphaltene fraction on wax crystallization was studied. Asphaltene fractionation on calcium carbonate was developed further to a column separation procedure, which yielded asphaltene fractions with even larger differences according to FTIR analysis. Wax crystallization was studied using differential scanning calorimetry (DSC), cross-polarized microscopy (CPM), rheometry, and pour point tests (PPT). Asphaltenes were found to change wax crystal morphology and decrease gel yield strength with increasing concentration. The effect on wax appearance temperature (WAT) was generally less. The greatest effect on WAT and pour point was made by *bulk* asphaltenes, which is the lowest polarity fraction from separation on calcium carbonate. *Irreversibly adsorbed* asphaltenes, containing significant amounts of carbonyl, carboxylic or derivative groups, induced the largest changes in wax crystal morphology. Still, high pour point and gel yield strength indicated low performance for this fraction. Overall, wax inhibition performance tended to be best for asphaltene fractions with low solubility and mixed functional groups. In isothermal titration calorimetry (ITC), unfractionated *whole* asphaltenes interacted more strongly with crystallized wax than asphaltene fractions *bulk* and *irreversibly adsorbed*. The findings indicate that wax crystallization is influenced the most by an ensemble of asphaltenes with different functional groups, rather than groups with more distinct properties.

1. Introduction

Current trends in crude oil production are towards higher depths, harsher environments, and increased field complexity. These trends can aggravate flow assurance challenges imposed by paraffin wax in the crude oil. Crystallized wax can cause issues both downhole and topside, which include flow reduction or plugging due to wax deposition, increased fluid viscosity, and restartability issues because of the formation of high strength waxoil gels [1]. Different thermal, mechanical, and chemical methods are usually taken for wax control, in particular the use of chemical additives such as wax inhibitors (WI) and pour point depressants (PPD) [2,3]. As new PPDs, the use of fractionated asphaltenes has been suggested [4]. A positive influence on gelation and gel yield strength of waxy crude oils has been attributed to asphaltenes [4–6]. Moreover, several patents exist for the use of asphaltenes as pour point depressants for shale oil [7–9]. In two preceding publications, asphaltenes were fractionated via newly developed procedures that involved asphaltene adsorption on calcium carbonate, as well as stepwise precipitation from bulk [10,11]. This article is a continuation of previous work, where the fractionation on calcium carbonate was developed further to a column separation procedure that yields asphaltene fractions with even larger property differences. The primary objective was to study the influence of various asphaltene fractions on a model waxy oil. This allows cross referencing of asphaltene properties from current and previous characterizations with their effect on wax crystallization. The goal is to determine which asphaltene characteristics are most crucial during wax crystallization, and hence improve the understanding of asphaltene-wax interactions.

Paraffin wax is a natural constituent of crude oil, which is defined as mostly straight, ring formed, and branched alkanes with 18 or more carbon atoms [1]. Wax crystallization is reported to take place in three steps, which are (i) nucleation, (ii) growth, and (iii) agglomeration [12]. The wax appearance temperature (WAT) is defined as the highest temperature, at which the crystallization of wax can be observed [13]. As the wax crystals grow in size, three dimensional interlocking of the crystals facilitates the formation of a solid like gel [14]. Paraffin wax crystals formed in organic solvents can exhibit plate shapes, needle shapes, and malcrystalline or dendrite like masses [15,16]. The waxes can be grouped into macrocrystalline and microcrystalline waxes, depending on the crystal shape [17]. Macrocrystalline wax has been reported to largely consist of low molecular weight *n*-alkanes that form predominantly plate shaped crystals with large hydrodynamic radii. Microcrystalline wax is considered to contain significant amounts of high molecular weight *iso*-alkanes and *cyclo*alkanes, leading to compact and round crystal morphologies with smaller diameters. As a consequence, macrocrystalline wax generally leads to the formation of strong gels, whereas microcrystalline wax accounts for in comparison weak gels [18].

The temperature at which a liquid loses its ability to freely flow due

increasing amounts of precipitated wax is referred to as pour point, as defined by ATSM D97 [19]. A pour point depressant (PPD) consequently refers to chemical additives, which can decrease the pour point. The term wax inhibitor (WI) will be used in a more general context in this study. It refers to chemical additives that can alleviate challenges associated with paraffin wax crystallization via one or more functionalities. PPDs function as crystal modifying substances through coprecipitation with the wax [20–22]. PPD polymers provide spatial hindrances during continued crystals growth, leading to the formation of distorted and more compact crystal shapes with lower hydrodynamic radius. This can further result in particle dispersions with lower viscosity, waxoil gels of lower yield strength, and prevention or delay of the formation of a solid like gel, a process also referred to as pour point depression. Asphaltenes have been noted to predominantly interact with the more polar or aromatic groups of a PPD [17]. In waxy crude oils, the presence of asphaltenes has been reported to enhance as well as diminish the effect of WIs and PPDs [23,24]. For example, synergistic effects between asphaltenes and maleic anhydride co-polymers (MAC) as well as ethylenevinyl acetate copolymer (EVA) have been reported [25–27].

Asphaltenes have been reported to be natural PPDs by many authors [5,6,23,25–34]. Still, the effect of asphaltenes has been discussed contradictorily [35]. Some authors state no synergistic interactions between wax and asphaltenes [36], and other authors report asphaltenes aggravating issues associated with paraffin wax [24,37]. Asphaltenes are defined via solvent properties, being insoluble in low molecular weight *n*-alkane solvents [38]. Due to this definition, asphaltenes can have greatly varying composition and properties depending on the crude oil of origin, which would in turn account for the contradicting reports. However, most reports agree on the following effects that asphaltenes can have on paraffin wax crystallization:

- 1 Asphaltenes can serve as nucleation sites for wax crystals, which can increase WAT [37], but also lead to more finely dispersed wax crystals [6,23].
- 2 Asphaltenes can cocrystallize with wax, which can alter crystal morphology and improve crude oil rheology [6,29,35,39].
- 3 It is mainly the aliphatic part of asphaltenes, which interacts with paraffin wax [29,39,40].
- 4 The dispersion degree of asphaltenes plays a crucial role during wax crystallization [5,30,31].

Several authors have investigated the effect of asphaltene properties on wax crystallization by using either asphaltenes originating from different crude oils [24,29] or fractionated asphaltenes [4,6,34]. In two of these cases, asphaltene fractionation has been conducted by dissolving asphaltenes in dichloromethane (DCM) and inducing stepwise precipitation with pentane [34,41]. In one case, asphaltenes were fractionated on silica gel and via reverse phase chromatography [4].

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